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Studies on photoelectrochemical storage cells using CdSe and SnS electrodes

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Abstract : Photoelectrochemical cells have been constructed for the conversion and storage of solar energy based on three-electrode system and redox storage cells. CdSe and SnS thin films were electrodeposited and were used in the storage cells. The performance of these cells was studied in the charging and discharging modes.

Keywords : Storage cell, energy conversion, energy storage.

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1. Introduction

In the recent years, photoelectrochemical cells have evoked much popularity as a renewable energy source because of some potential advantages over the conventional solid state devices *e.g.* in minimizing problems arising from lattice mismatch in controlling the barrier heights, easy method of fabrication, direct penetration of solar radiation to the active semiconductor surface and no requirement of antireflection coatings.

A number of review articles on photoelectrochemical (PEC) conversion and storage have appeared in the literature [1–3]. Rechargeable electrochemical storage cells and the storage electrode capable of undergoing reversible chemical change have been reported [4,5]. Various designs of PEC cells have been demonstrated and tested; the aim being to convert solar energy into suitable forms for more efficient use [6–12].

Redox battery systems have generated interest as a means for energy storage [13]. The oxidized species are developed in one half cell called as anodic compartment and the reduced species are formed in the other half cell called as cathodic compartment. A number of redox couples have been studied for such systems. They include Fe^{3+}/Fe^{2+} (HCl),

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Cr^{3+}/Cr^{2+} (HCl), Ti^{4+}/Ti^{3+} and Br_2/Br. Out of these couples, the Fe–Cr redox system [14] appears promising due to its high electrochemical potential (E = 1.18 eV). However, there are no reports on electrodeposited CdSe and SnS thin film electrodes used in energy storage systems.

In the present investigations, we report on the preparation of CdSe and SnS thin films by electrodeposition method. The PEC cells were formed by using CdSe and SnS as photoelectrodes and graphite as counter electrode and their current-voltage (output) characteristics were studied. To the best of the author's knowledge these films have been used for the first time in two confirgurations of rechargeable liquid junction cells as three-electrode and redox storage cells.

2. Experimental details

2.1. Preparation of CdSe thin films :

CdSe thin films were electrodeposited onto stainless steel substrates by the co-electrodeposition of cadmium and selenium from cadmium sulphate and selenium dioxide in sulfuric acid solution under galvanostatic condition at room temperature (27°C). The suitable composition of the bath was found to be 0.05M $CdSO_4$ – 0.01M SeO_2 at 2–3 pH, to furnish uniform, thick and good adherent films. These films were annealed at 500°C for 30 minutes in nitrogen atmosphere and then etched in diluted (10%) HCl, before being used as photoelectrodes in the storage cells.

The PEC properties of CdSe films were tested in dark, and under illumination, using tungsten filament lamp. A water filter was interposed between the lamp and the cell to prevent heating of the cell. Photovoltaic power output characteristics were obtained under a light intensity of 80 mW/cm^2. Spectral response of the cell in the wavelength range of 400–900 nm was studied.

2.2. Preparation of SnS thin films :

The SnS thin films were electrodeposited from the bath consisting 0.05M $SnCl_2$ – 0.01M $Na_2S_2O_3$ – 0.01M CH_3COOH as described in a previous work [15]. The photovoltaic activity of SnS thin film was tested by forming a photoelectrochemical cell with the Fe^{2+}/Fe^{3+} redox electrolyte under a light of 80 mW/cm^2 intensity and the output characteristics were obtained.

2.3. Three-electrode storage cell :

Schematic diagram of the construction of the three-electrode storage cell is shown in Figure 1. The two compartments of the cell, made of corning glass, were connected by a conducting bridge (3 cm in length) formed with agar-agar gel. The first compartment contains CdSe as photoelectrode (P), graphite as counter electrode (C) and 1M (Na_2S–S–NaOH) as redox electrolyte. The other compartment was kept in the dark, contains SnS as a

storage electrode immersed in 1M KCl. Key K_1 was kept closed and K_3 opened during charging of the cell. Key K_2 was closed intermittently to record the charging voltage. The charging current and voltage were recorded with time.

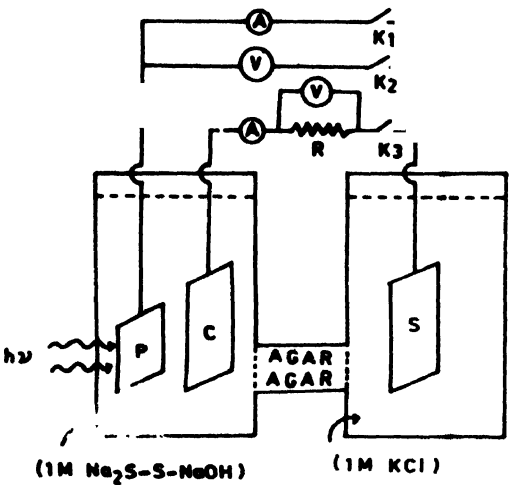

Figure 1. Photoelectrochemical storage cell, P-Photoanode either *n*-CdSe or *p*-SnS, C-counter electrode; S-storage electrode.

To obtain the discharging characteristics of the Cell, K_1 and K_2 were kept open and K_3 was kept closed. The discharging current and voltage were recorded with time using 1 KΩ load resistance.

2.4. Redox storage cell :

The redox storage cell was formed using SnS thin films as photoelectrode (P) and graphite (C) as counter electrode in the first compartment consisting of 0.1M ($FeCl_2$–$FeCl_3$) H_2SO_4 as redox-1 electrolyte. The second compartment consists of 1M (Na_2S–S–NaOH) as redox-2 electrolyte. A graphite electrode replaces the storage electrode (S) in Figure 1. The charging and discharging characteristics were obtained by recording the current and voltage with time.

3. Results and Discussion

3.1. Photovoltaic characteristics of CdSe and SnS based PEC Cells :

The photovoltaic output characteristics of the *as*-deposited CdSe and SnS thin films are shown in Figure 2. The power efficiency (η), fill factor (*ff*), short circuit current (I_{sc}) and the open circuit voltage (V_{oc}) of the PEC cells formed are listed in Table 1. The low efficiency of the cells could be due to high series resistance of the films. To improve the stability of the PEC cell formed with CdSe, a 50% mixture of 1M (KCl + NaCl) was added in the polysulfide.0 05M H_2SO_4 was added into the Fe^{2+}/Fe^{3+} electrolyte to improve the stability of the PEC cell formed using SnS electrode.

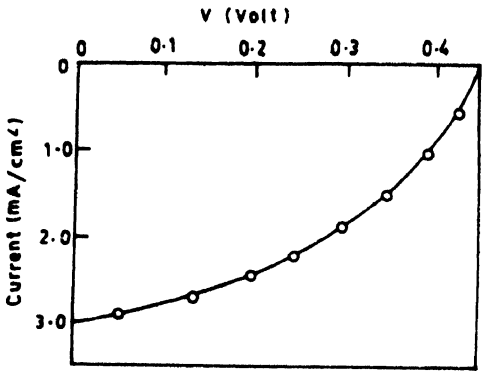

Figure 2(a). Photovoltaic output characteristics of *as*-deposited *n*-CdSe electrode.

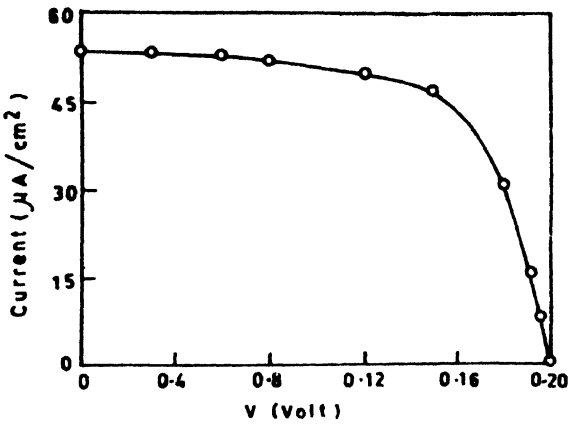

Figure 2(b). Photovoltaic output characteristics of *as*-deposited *p*-SnS electrode.

Table 1. The conversion efficiency, fill factor, V_{oc} and I_{Sc} of PEC cells.

Semiconductor/ electrolyte	V_{oc} (V)	(mA/cm^2)	Efficiency η %	Fill factor *ff* %
CdSe/1 M Na_2S–S, KCl + NaCl/C	0.45	3.0	1.5	55.5
SnS/0.1 M Fe^{2+}–Fe^{3+}, H_2SO_4/C	0.20	0.053	0.013	67 8

3.2. *Three-electrode storage cell :*

The variation of charging current and voltage with time in the charging mode of the cell are plotted in Figures 3 and 4 respectively. It is seen that during charging, current and voltage increase with time and attain the saturation values within 30 minutes.

The experiment was repeated using 1M NaCl and 1M KI in the storage compartment. The Values of I_{sc} and V_{oc} have been listed in Table 2. From our studies, it is

seen that KCl is more suitable electrolyte, giving greater values of charging current and voltage than NaCl or KI.

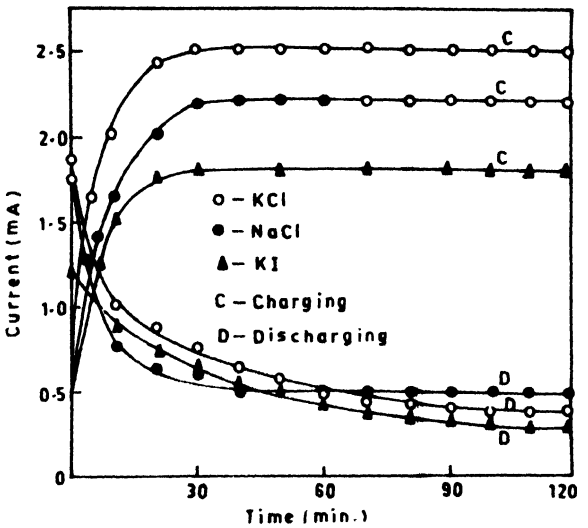

Figure 3. Variation of short circuit current with time in charging and discharging modes of the three electrode storage cell

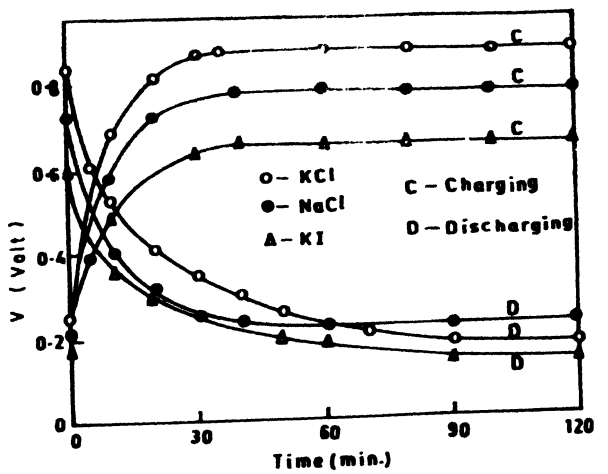

Figure 4. Variation of voltage with time in charging and discharging modes of the three-electrode storage cell.

The charged cell was allowed to discharge through 1 KΩ load resistance. The variation of discharging current through the load and the discharging potential across the load with time were plotted in Figures 3 and 4 respectively. It is seen that the current and voltage drop rather severely under load. This is attributed to resistance losses in the system, such as those in the photoactive layer, those in the electrolyte, polarization losses at the counter electrode and losses at the semiconductor-metal contact.

Table 2. Maximum change in current (ΔI_{sc}) and voltage (ΔV_{oc}) of the three-electrode storage cell in charging and discharging modes.

No.	Compartment I	Compartment II	Charging		Discharging	
			ΔI_{sc} (mA/cm^2)	ΔV_{oc} (V)	ΔI (mA/cm^2)	ΔV (V)
1	CdSe/1M Polysulfide	1M KCl/SnS	2.45	0.64	1.39	0.66
2	CdSe/1M Polysulfide	1M NaCl/SnS	2.16	0.55	1.06	0.50
3	CdSe/1M Polysulfide	1M KI/SnS	1.52	0.46	0.89	0 46

The associated reactions occurring at the respective electrodes under light are as follows :

$$CdSe + hv \rightarrow c^- + h^+ (hv > Eg)$$

due to the field,

$$e^- + h^+ \rightarrow e^- (bulk) + h^+ (surface)$$

(*i.e.* near the surface of photosensitive semiconductor electrode),

$$2\ h^+ (surface) + S^{2-} \rightarrow S (at\ CdSe)$$

(*i.e.* oxidation of the electrolyte would occur near the surface of semiconductor),

$$e^- (bulk) \rightarrow e^- (storage\ electrode)$$

(transfer through the back of semiconductor to SnS),

$$SnS + 2\ e^- \rightarrow Sn + S^{2-}$$

(*i.e.* reduction of the storage electrode)

forming a regenerative system, the net result being flow of electrons from photoanodic to the storage electrode through the external circuit. During the reduction process, the loosely bound tin element of the electrode or its precipitation at the bottom of the cell was not observed. This implies a stable system. The holes created at the surface of the photoelectrode cause oxidation of the polysulfide. The open circuit potential of the photoanode was –1.14 V versus SCE. The potential of the graphite electrode determined by S^{2-}/S_x^{2-} couple was found to be –0.61 V versus SCE.

In order that an electrode may function as storage electrode, its potential should be intermediate between the potential of the photoelectrode under illumination and that of redox couple in the electrolyte. SnS (the potential being –0.81 V versus SCE) may be used as storage electrode according to the following reactions in dark, indicating the spontaneous oxidation of tin.

$$2\ Sn + S^{2-} \rightarrow 2\ SnS + 2e^- (at\ storage\ electrode)$$

$$S + 2e^- \rightarrow S^{2-} (at\ counter\ electrode,\ C).$$

In the dark, when the storage electrode (SnS) is connected to the graphite counter electrode (C) of the PEC cell, the latter will act as anode and the current will flow in the reverse direction through the external load. The inherent resistance of the photoelectrode minimizes dark losses through the photoanode. The nominal relative concentration of the sulphur and sulfide within the photoelectrode and SnS compartments varies with degree of cell charging. The storage efficiency of the cell was found to be 28% under 80 mW/cm^2 solar radiation. The solar to electrical conversion efficiency estimated using the following equation was found to be 2.75%

$$\eta\% = \frac{(I \times V)_{maxi} \times 100}{80 \text{ mW}} \tag{1}$$

The low efficiency of the conversion of solar energy into the electric energy is mostly due to the photoconversion compartment and not due to the photoelectrochemical storage compartment.

Thus, it is possible to store current under illumination and derive the same in dark through the use of SnS as a storage electrode. The new drawback of the device is the lack of stability of the storage system. This is presumably due to diffusion of S^{2-}/S_x^{2-} through the agar-agar gel which visibly changes to yellowish is colour in about forty eight hours time. This diffusion of S^{2-}/S_x^{2-} into storage compartment lowers the negative potential of the storage electrode resulting in a decrease in storage efficiency which may be improved by seperating the two compartments by an ion specific membrane impermeable to sulfide ions.

3.3. Redox storage cell :

In order to investigate the storage ability of the cell, the variation of the open circuit voltage and short circuit current with time in the charging mode of polysulfide solution, are

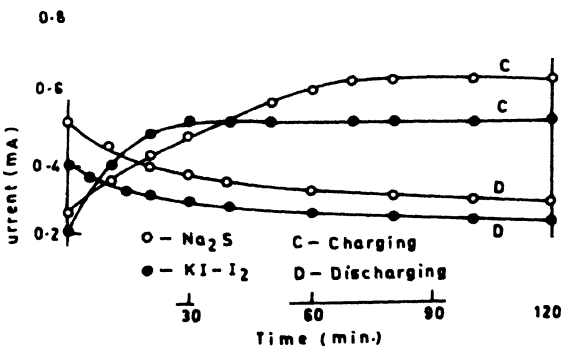

Figure 5. Variation of short circuit current with time in charging and discharging modes of the redox storage cell.

in Figures 5 and 6 respectively. It is seen that the saturation values of current and potential are attained somewhat later than in case of a three-electrode storage cell. However, the

steady staturation valiues are attained within two hours of charging (Table 3). The charging of the cell can be understood from the following reactions :

$$Fe^{3+} + e^- \rightarrow Fe^{2+}, \qquad \text{(Compartment I)}$$

$$S^{2-} + 2h^+ \rightarrow S, \qquad \text{(Compartment II).}$$

Thus, the electric energy is stored in the form of oxidized species of S^{2-}.

Table 3. Maximum change in current (ΔI_{sc}) and voltage (ΔV_{oc}) of the redox storage cell in charging and discharging modes.

No.	Compartment I	Compartment II	Charging		Discharging	
			ΔI_{sc} (mA/cm^2)	ΔV_{oc} (V)	ΔI (mA/cm^2)	ΔV (V)
1	SnS/0.1M Fe^{2+}–Fe^{3+}, H_2SO_4/C	Polysulfide/C	0.37	0.5	0.32	0.25
2	SnS/0.1M Fe^{2+}–Fe^{3+}, H_2SO_4/C	KI–I_2/C	0.30	0.40	0.17	0.26

Discharging of the cell was studied measuring the discharging current through 500 Ω load resistance and the voltages were measured across the load. From Figures 5 and 6 it is

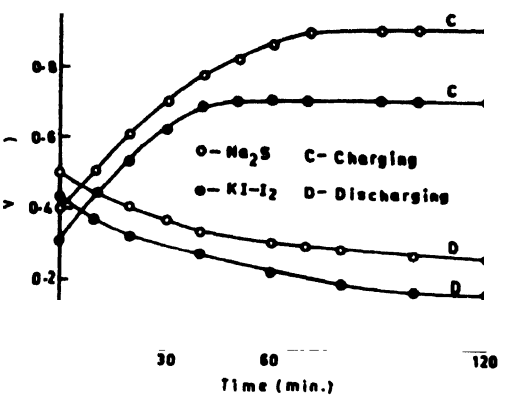

Figure 6. Variation of voltage with time in charging and discharging modes of redox storage cell.

seen that both voltage and current decrease with time and attain constant values after two hours discharge. The faster fall of current and voltage at the beginning of, the discharging mode may be due to resistance losses in the cell.

In the dark, the following reactions are associated at the respective electrodes :

$$Fe^{2+} \rightarrow Fe^{3+} + e^-, \qquad \text{(Compartment I)}$$

$$S + 2e^- \rightarrow S^{2-}, \qquad \text{(Compartment II).}$$

Similarly, the charging and discharging of the cell

$$SnS/Fe^{2+} - Fe^{3+}, 0.05M\ H_2SO_4/C/KI\text{–}I_2/C$$

were also studied (Table 3).

4. Conclusions

In this investigation, CdSe and SnS films were prepared by a simple electrodeposition technique and were employed as electrodes in two configurations of the storage cells. The conversion and storage of solar energy in the demonstrated cell is possible and the electric power can be regenerated without altering the nature of the electrolyte.

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